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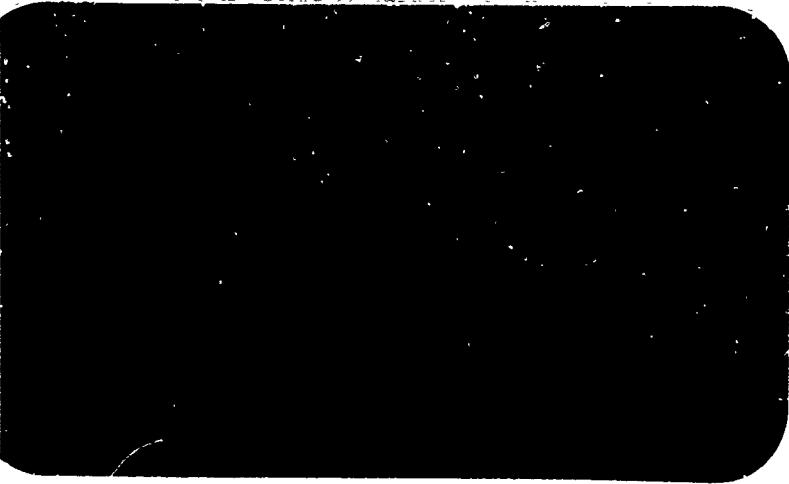
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Development of an Improved
Process for the Catalytic Oxidation
of Atmospheric Contaminants
in Submarines

Phase II, Assignment 73 107
MEL R&D Report 449/65
January 1965

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ABSTRACT

Studies in the development of an improved catalytic oxidation process reveal that polluted air causes other problems along with the corrosion which has been experienced in submarines.

CO/H₂ Burner troubles are explained by data showing inhibition of Hopcalite due to adsorption of CO₂ and organic halides and showing catalyst granules turning to dust because of thermal fracture.

Minimization of air pollutants is necessary, and preprocessing to remove certain materials before the catalytic oxidation is a necessary part of air purification.

MEL Report 449/65

ADMINISTRATIVE INFORMATION

The work reported herein was performed under MEL Assignment 73 107, Sub-project S-F013 08 03, Task 4095. The project was authorized by Bureau of Ships letter Serial 649G-1264 of 9 July 1963 and is based upon a proposal forwarded by MEL letter NP/10330(833), Assignment 73 107 of 30 August 1963.

TECHNICAL REFERENCES

- 1 - Calvert, W. R., "Development of an Improved Process for the Oxidation of Atmospheric Contaminants in Submarines," MEL R&D Phase Rept 118/64, Nov 1964
- 2 - MEL Conf ltr NP/10330(733), Assigt 73 107, to Chief, BUSHIPS (Code 649G), Jan 1966
- 3 - MEL ltr NP/10370(833), Assigt 73 114, covering the work to be performed to provide nuclear submarine forces with criteria for selection of materials to be used in original construction and/or overhaul, 27 Feb 1964
- 4 - BUSHIPS ltr SSN/SSBN 9380 ser 649G2-961 of 28 May 1965
- 5 - Ross, P. H., Jr., "Examination of Return-from-Aft Ventilation System in USS JAMES MADISON (SSBN 627) and USS SAM RAYBURN (SSBN 635)," MEL Tech Memo 344/64, Jan 1965
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- 7 - Fields, D. E., "Investigation of Sources of Chlorinated Hydrocarbons on Nuclear Submarines and Inspection of Corrosion Resulting from the Combustion of These Materials in CO-H₂ Burners," NRL Trip Rept 6120-507:DEF:hlw, NRL Problem C08-18, task group rept, BUSHIPS Project S-F013 08 03, 10 Sep 1964
- 8 - Calvert, W. R., "Report on Task Group Visits to Three Shipyards," MEL memo from Code 833 to Code 500, 24 Sep 1964
- 9 - Press release, American Aviation Publications, Inc., 1001 Vermont Ave N.W., Washington, D.C., 20005, in "missiles and rockets," 13 Sep 1965, p. 26

ERRATUM NOTE

In MEL Report 118/64, reference 1, page 5, paragraph 2.4.3, first line, please make the following change "The commercial catalyst, No. 1, Table 1, was evaluated by the same procedure..."

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Submarine Corrosion Sites

DEVELOPMENT OF AN IMPROVED PROCESS FOR THE
CATALYTIC OXIDATION OF ATMOSPHERIC CONTAMINANTS IN SUBMARINES

1.0 THE AIR-PURIFICATION/CORROSION PROBLEM

The previous report¹ describes air-purification equipment and materials involved in corrosion, along with data from testing of oxidation catalysts. This report continues the assembling of information and broadens the definition of the problem to include distribution of corrosion within the submarine's system. Organic halide reaction in the CO/H₂ burner is strong evidence of incompatability. This directs attention to similar reaction which may be involved in trouble found elsewhere within the submarine.²

"Ventilation" distributes corrosion within nuclear submarines. This is not the "ventilation" of common definition since it circulates but does not replace foul air. The needs within the enclosed atmosphere are better described by "air-maintenance." "Ventilation" employs the concept which permits accumulation of contaminants up to trace quantity levels, removing enough to prevent dangerous accumulation, and this was considered to be a more practical approach than to provide completely purified air to replace foul air. The trace quantities become askew because of pollution not accounted for in the design of the system. Major pollution occurs as emissions from materials of construction, maintenance, and normal operations. Some pollution causes severe corrosion, some is toxic, and some can be tolerated.

An abrupt change of thinking comes with the realization that the enclosed air is used as the media through which pollutants are transferred from sources to the air purification equipment, and that is expected to keep this same media suitable for use by the crew and by sensitive electronic (and other) submarine gear. The main mass of air is being polluted while a fraction of it is processed to remove a few kinds of contaminants. "Ventilation" has sometimes made the enclosed air worse instead of better.

¹Superscripts refer to similarly numbered entries in the Technical References at the beginning of this report.

A high dilution (circulation) rate averages the pollutants obscuring any correlation of test results with physiological or other effects due to exposure of crew or gear to higher concentrations near sources. In addition, some pollutants have strange effects on the analytical instrumentation with resulting unresolved troubles and doubtful data.

1.1 Corrective Measures. This Laboratory is active in three programs to provide corrective measures, with objectives as follows:

- The first is to eliminate the sources of pollutants. A search is under way to find acceptable adhesives, etc for submarine construction.³
- The second is to provide help needed to alleviate existing corrosive effects. Alkali-impregnated paper filters were provided to three submarines. This effort has been superceded by the BUSHIPS program of installing filter beds made of granular lithium hydroxide. The possible benefit obtainable from neutralizing CO/H₂ Burner effluent, by combining it with effluent from CO₂ Scrubbers, is under study.⁴
- The third is to develop a process of catalytic oxidation of CO and H₂ which avoids decomposition of organic halides into corrosive materials.¹

1.2 Scope. Progress in the second phase of the third program includes details from the study of:

- Catalytic oxidation of CO and H₂ while organic halides are present.
- Thermal fracture of Hopcalite and LiOH granules, producing dust.
- Adsorption by catalysts and by molecular sieves.

The discussion leads to recommendations for future air-maintenance systems in submarines.

1.3 Background. This Laboratory's approaches to the problem and the Bureau of Ships suggested modification of the catalytic process are now viewed in a different way as a result of previous work.

1.3.1 "Use of a catalyst different from that now used." In addition to ability to oxidize, the catalyst will not produce dust and will be better to handle and to store. One or more catalysts are acceptable, and if circumstances are right during their use, the organic halide corrosion will be minor.

1.3.2 "Operation of the system at temperatures lower than now used." Least heat input is preferred. Minor decomposition of organic halides limits temperatures to below 300 F,* an arbitrarily chosen value based on testing experience.

1.3.3 "Use of chemical reactants and adsorbents to prevent undesired components from entering and/or leaving the system." The Bureau of Ships suggested use of a preadsorber, such as silica-gel to remove moisture, now becomes a necessary pre-processing to remove damaging species of pollutants, such as Refrigerants 11 and 12, methyl chloroform, amines, etc, when present.

2.0 APPARATUS

The apparatus previously described¹ has been modified slightly to permit liquid vaporization so that catalytic oxidation of CO and H₂ can be studied in the presence of vapors from methyl chloroform, Refrigerant 11, etc.

A chamber was added in such a way that adsorption alone can be studied. This same apparatus, Figure 1, can be used to study adsorption followed by catalytic oxidation. Organic halides were measured employing hydrogen flame ionization. In earlier work a Perkin-Elmer 213B hydrocarbon detector was used. In later work a gas chromatograph (Beckman GC-2) was used. Both hydrogen and organic halides were measured by gas chromatography using a thermal conductivity cell in series with a hydrogen flame ionization detector.

*Abbreviations used in this text are from the GPO Style Manual, 1959, unless otherwise noted.

The apparatus for studies of dusts from catalyst and LiOH were: U. S. Standard Sieves and Tyler ROTAP sieve shaker, a balance, and a heat-treatment furnace.

3.0 DATA

3.1 Samples. Samples of Hopcalite (with LiOH) were obtained from shipboard CO/H₂ burners. One was a new mixture and another had been in use for 250 hours. One other sample, Figure 2, was taken because of a complaint regarding persistently high back pressure across a catalyst chamber.⁶

3.2 CO/H₂ Oxidation. Data and procedures have been described¹ for Hopcalite alone and in the absence of organic halides. Because LiOH was added to alleviate corrosion effects from air-borne halogen compounds carried into the catalytic oxidation reaction zone of the CO/H₂ burners, the oxidation studies included it, with methyl chloroform and Refrigerant 12, in the test stream of simulated submarine air. Hydrogen and CO contents of effluent after reaction were measured to show changes at various catalyst temperature levels. Data curves are shown in Figures 3 and 4.

3.3 Dust from Thermal Fracture. Sieve test data, Table 1, show the particle size decrease after heat treatment of two catalysts and LiOH granules.

3.4 Decomposition Products. During catalysis and when measuring effluent components, the products from decomposition of organic halides show as a CO signal in the LIRA analyzer. Some toxic materials (phosgene and other carbonyls) could be expected in these products that are hydrolyzed to corrosive materials. Data from long path infrared analysis are shown in Table 2. Examples of chemical reactions probably occurring in submarines are given in Appendix A.

3.5 Adsorption Studies. Adsorption (and oxidation) curves from tests with catalysts and molecular sieves are shown in Figure 5. Effluent changes were measured while processing a simulated submarine air stream through the adsorption chamber and apparatus of Figure 1.

Table 1
Thermal Fracture Data*

[From a study comparing Hopcalite, LiOH,
and one of the platinum-alumina catalysts.]

Particles Passing ----	Standard Sieves					
	square hole sizes, inches					
	-	0.132	0.094	0.066	0.056	0.028
Particles Retained on-	0.132	0.094	0.066	0.056	0.028	Pan
Grams per 100 grams of sample						
<u>Hopcalite MnO₂/CuO granules</u>						
before heating	31.9	54.0	6.5	0	3.0	4.6
after glowing (1400 F)	7.7	23.1	19.3	0	15.4	34.5
after 1100 F heat treatment	7.8	15.5	14.6	3.8	12.4	45.9
<u>No. 1 Catalyst</u>						
<u>Pt/Al₂O₃ 1/8 in. spheres</u>						
before heating	0	42.2	54.2	0	1.6	2.0
after glowing (1400 F)	0	41.8	53.5	0.4	1.7	2.6
after 1100 F heat treatment	0	42.7	52.1	0.6	2.2	2.4
<u>LiOH H₂O granules</u>						
before heating	30.0	41.6	23.4	0.8	0.4	3.8
after 800 F heat treatment (melts at 842 F, with frothing)	9.3	31.6	26.0	3.2	2.2	27.7

*Samples were sieve tested (15 minute ROTAP), heated as shown, cooled, and sieve tested again.

Table 2
Long-Path IR Analysis of Gas Samples

[Collected after catalytic oxidation during periods of product CO (LIRA) while there was no CO input.]

Test Stream	Organic Halide Analysis		
	LIRA CO - ppm	P-E 213B ppm (CH ₄)	Materials Found by Analysis with Long-Path IR
<u>250-HR Mix From SSBN 635 at 685 F</u>			
Input	None	100 50 Sum = 150	Refrigerant 12 (CCl ₂ F ₂) Methyl chloroform (CH ₃ CCl ₃)CO ₂ H ₂ O
Effluent	9	90 (Sum)	Refrigerant 12 and vinylidene chloride (CH ₂ :CCl ₂)CO ₂ H ₂ O, with uncertain identification of minor components
<u>New Mix From SSN 595, at 950 F</u>			
Input	None	4660	Methyl chloroform, CO ₂ , H ₂ O
Effluent	100+	825 (Sum)	Vinylidene chloride (major) tri-chloroethylene (CHCl:CCl ₂) CO (trace), CO ₂ , H ₂ O, etc.

4.0 DISCUSSION OF TESTS

4.1 Hopcalite Alone. A higher temperature is needed to oxidize hydrogen in the presence of chloro- and fluoro-hydrocarbons (C-F-H), Figure 3(a). These materials are inhibitors extending the effect of CO₂ previously shown.¹

Adsorption of CO_2 , CO, and Refrigerant 11 by Hopcalite is shown in Figure 5(b). This explains the low-temperature inhibition of the catalytic oxidation of CO in the presence of C-F-H, Figure 4(a). Adsorption of endothermic materials inhibits exothermic oxidation.

4.2 Hopcalite with LiOH in It. The samples of new and used (250 hr) Hopcalite are shown to be alike, in Figure 3(b), for the oxidation of hydrogen. These curves show incomplete oxidation of hydrogen, which was complete during a brief period when the C-F-H was absent. This same effect is shown in Figure 3(c), testing with lower hydrogen input concentration. The C-F-H effect during CO oxidation is similar, Figure 4(b). In the CO oxidation, three "blanks" were found. The third blank increases with heat input increase, obscuring the measurement of CO oxidation.

4.3 Thermal Fracture. The thermal fracture of Hopcalite and LiOH, Table 1, explains the dust emission from the CO/H_2 burner. During the periods when the burner's heaters are on, the granules in the catalyst chamber are heated. When the heaters are off, the granules fracture as they cool. The No. 1 catalyst is resistant to this thermal fracture and will not emit dust in large quantities.

The melting of LiOH at 842 F, with frothing, explains disappearance of this material from hot catalyst chambers and the loss of catalyst activity.

The LiOH granules fracture easily, a fact that explains the large amount of white material in the smaller-size fractions seen in Figure 2.

4.4 Decomposition Products. Decomposition products from the organic halides (C-F-H) result in analytical problems because of effects on the instruments. The LIRA data, Figure 4, show three "blanks." Blank I is normal, being caused by water from H_2 oxidation. Blank II is caused by decomposition product accumulation which changes infrared light transmission, and Blank III is caused by products carried in the sample stream. The amount of Blank III increases as concentration of C-F-H increases when heat input to these materials is sufficient. Such increase is shown in the LIRA CO column of Table 2. Blank III may include product CO from partial oxidation of hydrocarbons which exhibit endothermic tendency.

4.4.1 The Perkin-Elmer 213B hydrocarbon detector was fouled in several ways by the decomposition products and by methyl chloroform samples and standards tested at room temperature. During continuous stream analysis with this instrument, the samples gave drifting and fluctuating signals. Pressure regulators made of aluminum alloy corroded, and white salts were found under the regulator diaphragm, in valves, and in capillary tubes. Its flame ionization detector required frequent cleaning because of accumulations which altered its electronic circuitry. After abandonment of continuous stream analysis in favor of small samples (gas chromatography), the frequency of trouble became tolerable.

4.4.2 For the long-path infrared tests, the C-F-H concentration in the sample was increased to enter within the field of sensitivity of this kind of instrumental analysis. Even so, resolution and identity of products of decomposition was obscured. Condensation and hydrolysis in the high moisture content of these samples cause separation and changes during conveyance of samples to the instrument.

4.5 Adsorption/Catalysis. The organic halides in the submarine's air make Hopcalite more adsorbent than catalytic, as shown in Figure 5. These curves also show that the No. 2 (Pt/Al₂O₃) catalyst¹ is only briefly adsorbent and an excellent catalyst under the circumstances of these tests. A further change in circumstances may inhibit this catalyst too. For this reason the contemplated replacement of Hopcalite by a catalyst similar to No. 2 requires detailed consideration of circumstances in its use, to avoid improper performance. For example, Figure 5(c) shows oxidation of CO and H₂ with no apparent effect on Refrigerants 12 and 11 in this test apparatus. This result may be quite different in the operation of a Mark IV CO/H₂ burner.

5.0 DISCUSSION OF SUBMARINE VENTILATION

5.1 Corrosion. The corrosion from organic halides is not new. The U. S. Navy has recognized the fact for at least two decades, rejecting use of these materials in hydraulic fluids.* Extensive use of fire-retardant solvents in adhesives, etc, was probably not expected when the ventilation system was designed. Refrigerating gases are in hermetically sealed units and are therefore not emitted as pollutants until leaks occur and when maintenance is necessary. A search for materials of construction which may result in corrosion was made by a task group,^{7,8} in August 1964.

5.2 Distribution of Pollutants. Nuclear submarine patrol reports list experiences related to distribution of dust and corrosive gases. It is obvious that toxic and damaging pollutants should not be distributed through the air which "blankets" the crew and sensitive equipment. Distribution of purified air is preferred. The foul air intake to purification equipment is preferably from space near sources which emit pollutants. Minimized distribution of pollutants should lead to many improvements in problem areas within the submarine's system.

5.3 Filtration of Dusts. Filtration to remove dusts is a requirement for future air-purification processes, and it is preferred that an essentially dust-free filter will be found at scheduled cleaning time, rather than one loaded with difficult-to-handle-and-otherwise-objectionable particulates.

5.4 Regenerable Adsorption. Adsorption on inorganic solids, such as the molecular sieves, is suggested as a means for removal of more kinds of contaminants. This can be viewed as a process which exposes prepared surfaces to the foul air for the purpose of attracting and retaining the contaminants, prior to controlled release and disposal to the sea during subsequent repreparation of the adsorbent surfaces. The adsorption of CO_2 and refrigerant gases by 13X molecular sieves is shown in Figure 5.

6.0 CONCLUSIONS FROM TESTING

Some of the troubles experienced in the operating of CO/H_2 Burners are explained by the inhibiting effects from CO_2 and from organic halides which are adsorbed at low temperatures. Desorption and oxidation occur as the Hopcalite is heated. To achieve complete oxidation of hydrogen, the required heat input increases as the concentration of inhibitors increase. CO oxidation is obscured by products from the organic halides. Thermal fracture causes granules of Hopcalite and LiOH to turn into dust. At least one of the known catalysts is resistant to thermal fracture. This permits elimination of the dust emission from the burners.

With organic halide contaminants minimized and kept under control trace quantities may be tolerable, if existing Mark IV CO/H_2 Burners are modified to employ a platinum-alumina catalyst and are operated at low temperatures for the purpose of oxidizing CO and H_2 . Others⁹ favor a platinum metal catalyst.

CO_2 , hydrocarbons, organic halides, and other contaminants can be removed to the sea by preprocessing the foul air employing regenerable adsorption, in future submarine air maintenance equipment.

7.0 RECOMMENDATION

Toxic and damaging airborne materials must be minimized in submarines and kept under control. This applies to measures that can be taken during construction and repairs and includes changes in CO₂ Scrubbers to avoid amine emissions and in CO₂/H₂ Burners to avoid dust and corrosive gas emissions. Shipboard burners should be equipped with a different catalyst as soon as possible.

Capabilities of integrated air-maintenance equipment for future submarines should include removal of all contaminants and excess heat to the sea, oxygen replenishment, pressure/volume control, heating for comfort, and distribution of processed air to the crew and to sensitive equipment. To do this, fundamental concepts need revising.

8.0 FUTURE WORK

Future work described in the previous report¹ will proceed after a Mark IV CO/H₂ burner becomes available along with provisions needed for the modification and a realistic evaluation to assure proper performance under conditions which will exist in submarines.

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Gas AnalysisCO and CO₂ by Nondispersive Infrared AnalyzersH₂ by Gas Chromatograph

Hydrocarbons by Hydrogen Flame Ionization Detectors

Moisture by Aminco % RH Meter

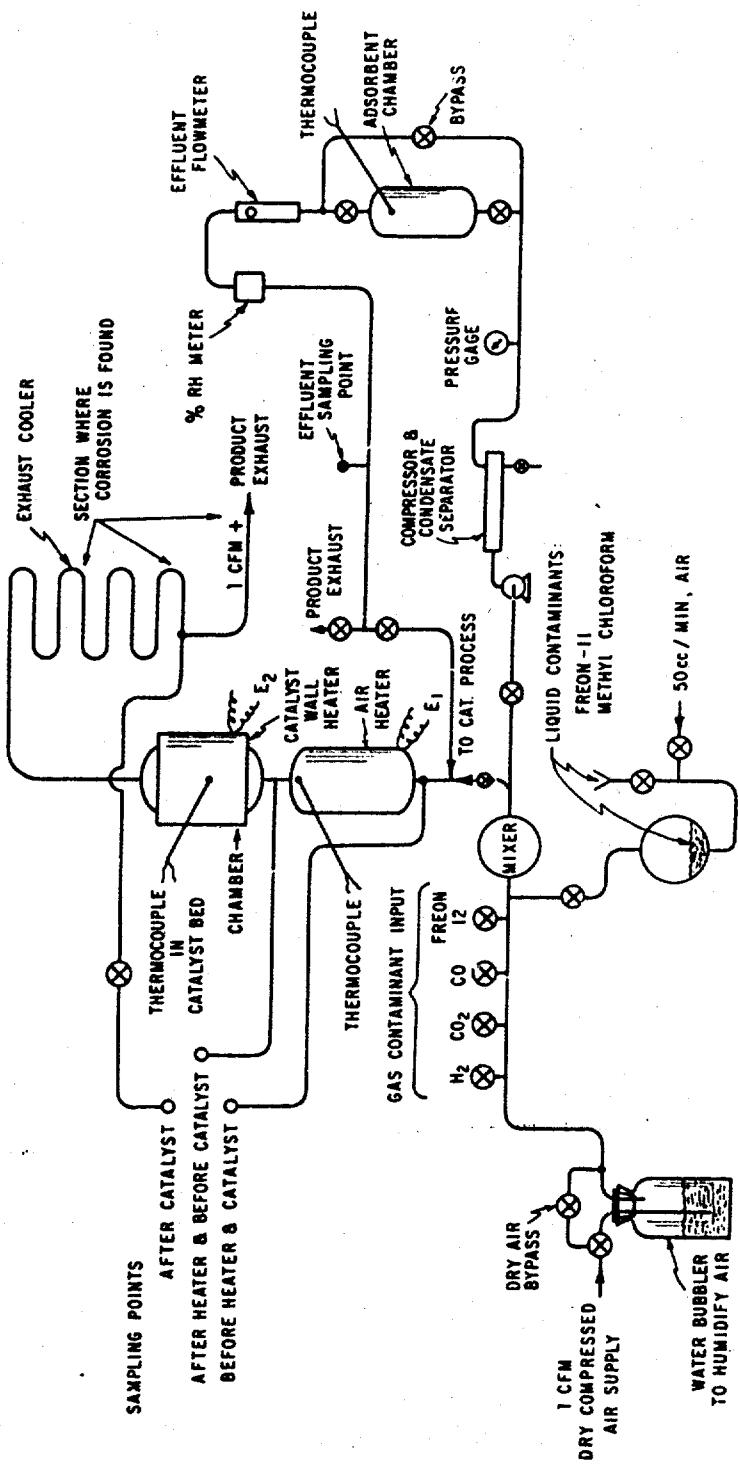


Figure 1
Flow Diagram of Experimental Catalytic
and Experimental Adsorption Processes

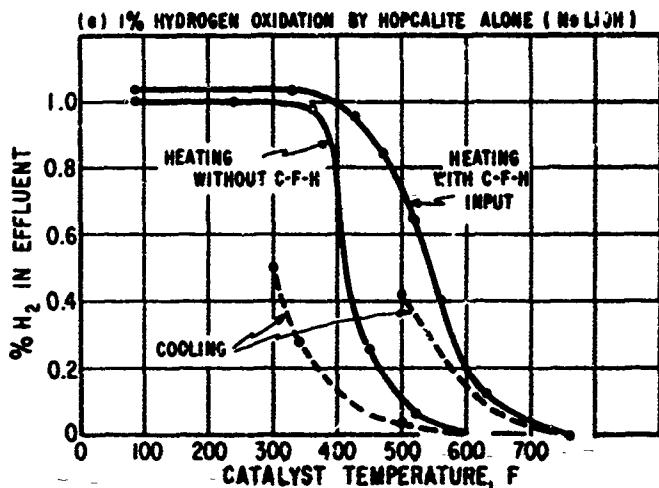
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Note the increased number of white LiOH particles as their size decreases.

Figure 2
Sample: Mixture of Hopcalite and LiOH
A Complaint Mixture from a CO/H₂ Burner

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Legend (for Figures 3 and 4)

Test Stream

Concentrations of CO and H₂ as shown by curves were included in the simulated submarine air along with 50% RH, 1% CO₂, 100 ppm Refrigerant 12, and 50 ppm methylchloroform. CFM through catalyst = 1.1; depth of bed 3.5 inch, FPM through catalyst = 140; volume of bed 3.78 cu. inch. Heaters: air and catalyst at 600 F; pressure = 1 atmosphere.

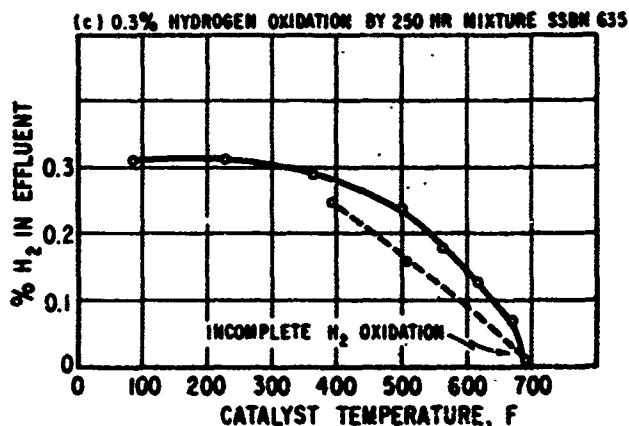
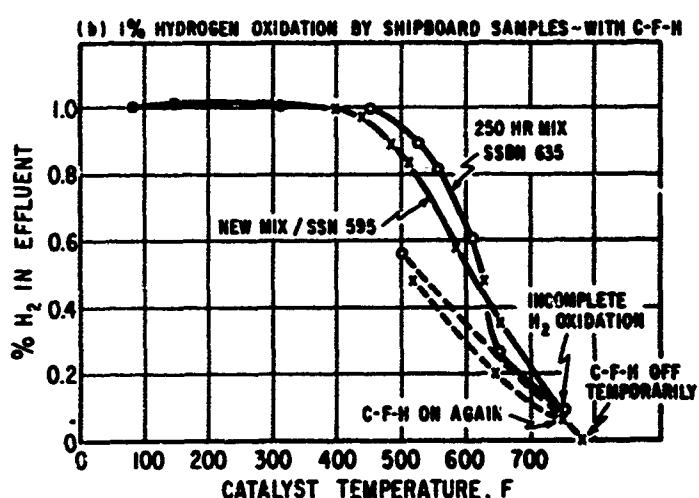
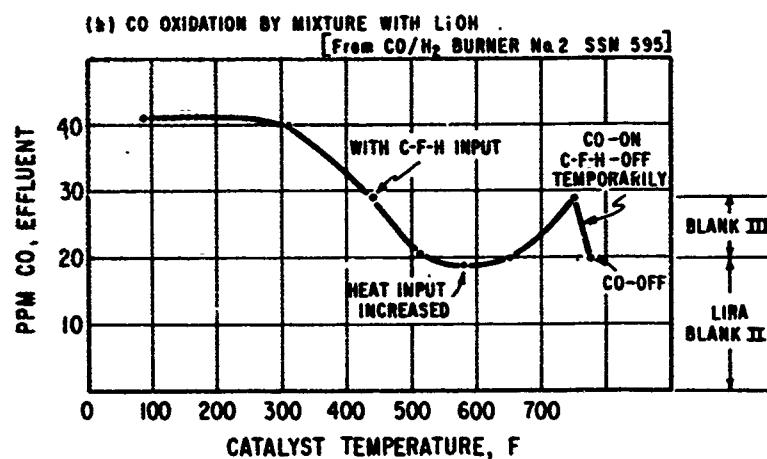
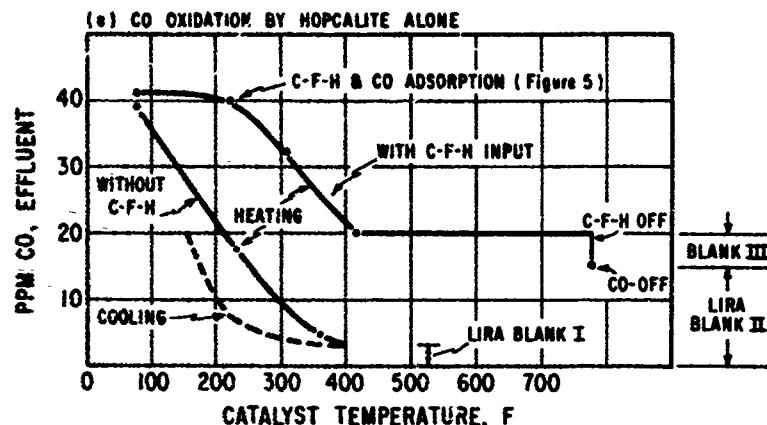


Figure 3
Hydrogen Oxidation
Showing Need for High Temperatures
and the Incomplete Hydrogen Removal
When Chloro- and Fluoro-Hydrocarbons
(C-F-H) Contaminants Pass Through the
Hopcalite + LiOH Mixtures

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Temporary LIRA Blanks

- Blank I - The LIRA is sensitive to water product from H₂ oxidation.
- Blank II - With CO input off, the blank is high after testing effluent containing C-F-H products. The LIRA signal returns to zero after overnight sweep-out with air.
- Blank III - With C-F-H input off and CO input on, the CO signal decreases. This blank increases as heat input increases, and may be product CO.

Figure 4
CO Oxidation
Showing Product CO When
Chloro- and Fluoro-Hydrocarbons (C-F-H)
Contaminants Pass Through Hopcalite Alone
and/or Hopcalite + LiOH Mixture

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Concentrations of contaminants in the simulated air are as shown in the curves. 50% RH stream pressurized to 30 psig with condensate separation resulting in 29% RH at pressure. CFM through adsorbent 0.85; depth of bed 5.4 inch. FPM through adsorbent 28.9; volume of bed 23.0 cu. inch.

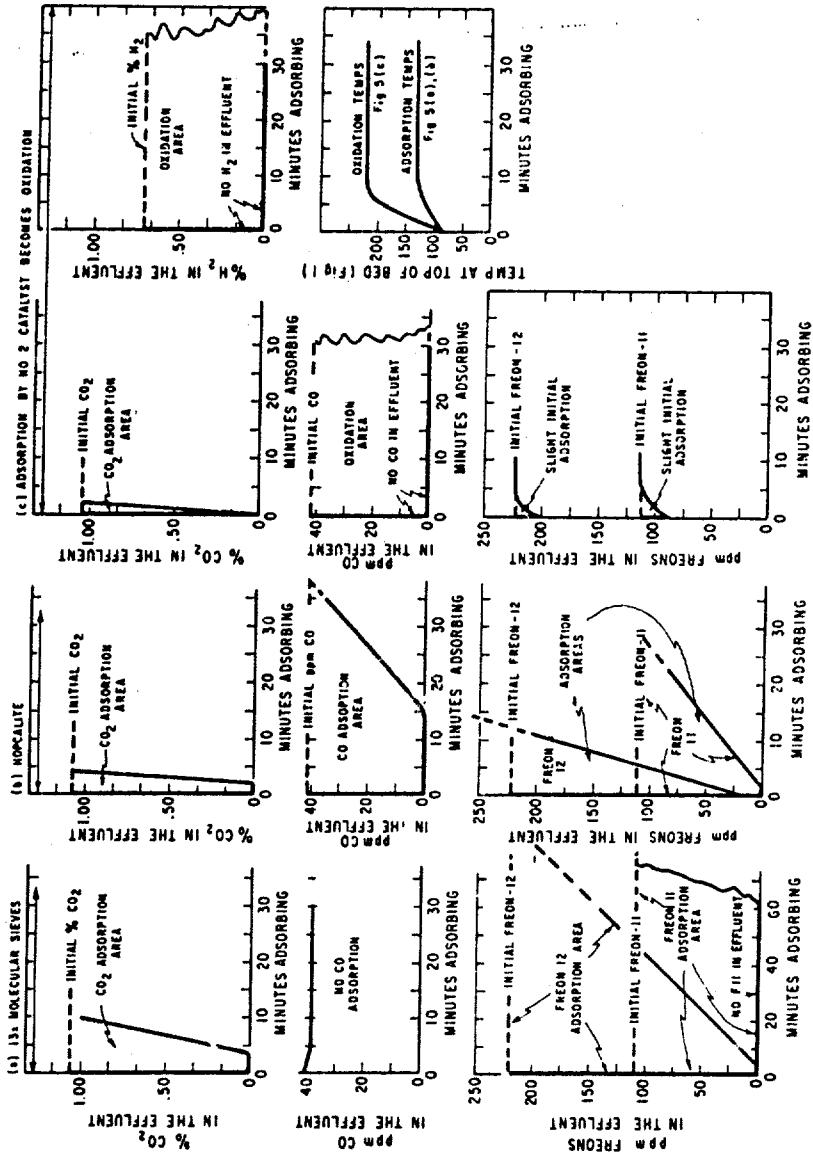


Figure 5 - Simultaneous Adsorption Curves from Study of Molecular Sieves and Catalysts

Appendix A

Examples of Chemical Reactions Probably Occurring
in CO/H₂ Burners and Other Submarine Corrosion Sites.Catalytic Oxidation/Decompositions

1. $2\text{CH}_3\text{:CCl}_3$ $\xrightarrow[\text{Heat}]{\text{Air}}$ $\text{CH}_2\text{:CCl}_2$ + CHCl:CCl_2
methyl chloroform vinylidene trichlorethylene
chloride
+ $\text{H}_2\text{O} + \text{HCl} + ?$ a miscellany
of partial
oxidation
products.
2. $\text{CH}_2\text{:CCl}_2$ $\xrightarrow[\text{Heat}]{\text{Air}}$ COCl_2 (phosgene) + CO + $\text{H}_2\text{O} + ?$
3. CHCl:CCl_2 $\xrightarrow[\text{Heat}]{\text{Air}}$ $\text{COCl}_2 \cdot \text{COCl}_2$ (oxalylchloride) + HCl + ?
4. Amine or NH_3 $\xrightarrow[\text{Heat}]{\text{Air}}$ Nitrogen oxides, amino- and
nitro-halides, etc

Hydrolysis on Moist Metals, with Salt Formation

5. $\text{COF}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \text{CO} + 2\text{HF} \xrightarrow{\text{Metal}} \text{CO} + \text{H}_2 + \text{Metal fluorides}$
6. $\text{COCl} \cdot \text{COCl} + \text{Fe} \xrightarrow{\text{H}_2\text{O}} 2\text{CO} + \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
7. $2\text{FeCl}_3 \cdot 2\text{H}_2\text{O} + \text{COCl}_2 \xrightarrow{\text{H}_2\text{O}} 2\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{CO}$
8. $\text{Al} + \text{CH}_3\text{:CCl}_3 \xrightarrow[\text{room temp}]{\text{Air & H}_2\text{O}} \text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{CO} + \text{CO}_2$

Heat Decomposition on Steam Pipes and Other Hot Surfaces

9. $\text{CCl}_2\text{F}_2 \xrightarrow[\text{Heat}]{\text{CO}_2} \text{COCl}_2 + \text{COF}_2$

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY NAVSHIPS
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13. ABSTRACT

Studies in the development of an improved catalytic oxidation process reveal that polluted air causes other problems along with the corrosion which has been experienced in submarines. CO/H₂ burner troubles are explained by data showing inhibition of Hopcalite due to adsorption of CO₂ and organic halides and showing catalyst granules turning to dust because of thermal fracture. Minimization of air pollutants is necessary, and preprocessing to remove certain materials before the catalytic oxidation is a necessary part of air purification.

(Author)

Security Classification Unclassified

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Habitability in Submarines Halogenated Hydrocarbons Air Pollution by Air Contaminant Removal Catalysts Adsorbents						

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